

1/07/04

10/532416  
JC12 Rec'd PCT/PTC 22 APR 2005

A METHOD OF PREPARING LUBRICANT ADDITIVES (VARIANTS)

(Specification as published)

Field of the Invention

The present invention relates to the field of petrochemistry, more particularly to -

5 molybdenum compounds comprising sulfur and their use as additives in lubricating materials for reducing friction coefficient.

Background of the Invention

It is well-known that in order to reduce fuel consumption and the wear of machine parts during friction, antifriction additives (friction modifiers) are introduced into lubricating oils. It 10 is also known that oil-soluble complex molybdenum are used as the friction modifiers, which compounds include sulfur, nitrogen or phosphor atoms as ligands.

Thus, for example, in US Patent [1] a method is described for preparing lubricating oil additives based on tetraalkyl(alkenyl)ammonium thiomolybdate, improving the antifriction properties of the oil. The use of relatively hard-to-obtain and expensive alkyl and alkenyl 15 groups produced from vegetable oils and fats, for example, cacao or soybean oil, as constituents of one of the initial components, and namely a tetraalkylammonium halogenide, relates to drawbacks of the proposed method.

A method is known [2] in which additives to lubricating oils are prepared by reacting a sulfur-comprising organic compound, having an active hydrogen atom, with molybdenum 20 pentachloride. The product isolated as a result of the reaction contains 3% of molybdenum and about 1% of chlorine, which is undesirable for ecological reasons and because of the possible corrosive activity of the product.

A molybdenum-comprising additive to lubricating oils, which exhibits antifriction and 25 antioxidation properties, is prepared as described in US Patent [3], in three steps, wherein in the first step a reaction is carried out of a triglyceride of vegetable oil with a nitrogen-comprising compound, then in the second step the product of the first step is reacted with a molybdenum compound, and in the third step the product of the second step is reacted with sulfur or a sulfur-containing compound. The relatively complex manner of synthesis (multi-stage process, the presence of an inert atmosphere, rigid limitation of the temperature ranges) should be 30 considered as drawbacks of the method.

Methods [4,5] are known, where oil additives based on dithiocarbamyl complexes of molybdenum are prepared. These additives are polyfunctional (including antifriction properties), but their synthesis is very complex and involves the use of toxic reagents, e.g., carbon disulfide.

5 A method is known, in accordance with which an additive to oils is prepared based on a mixture of a friction modifier (nitrogen- or oxygen-comprising organic compound) and a trinuclear sulfur-containing molybdenum complex comprising dithiocarbamine groups as the ligands [6]. The complex makeup of the additive and the multi-stage synthesis of the organomolybdenum compound are disadvantages of the method.

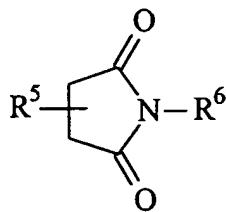
The most similar analog of the claimed invention is the method [7], in which an antifriction additive is prepared in the form of chemically modified nanosized particles of molybdenum trisulfide. In this method, the nanosized particles of molybdenum trisulfide are prepared by forming inverted microemulsions of the "water-in-oil" type, stabilized by 10 surfactants, and comprising water-soluble salts of molybdic acid in an aqueous phase, converting them into salts of thiomolybdic acid by reacting with hydrogen sulfide and subsequent isolation of nanosized particles of  $\text{MoS}_3$ , preliminarily processed with modifying compounds. As a result, nanosized particles of molybdenum trisulfide are obtained, which are stable in hydrocarbon media, including oils, and which exhibit high effectiveness as antifriction 15 additives. The low technological effectiveness of synthesis of the additive, which is related to carrying out the process in strongly diluted organic solutions and to the use of hydrogen sulfide as the reagent, should be considered as drawbacks of this method.

20 The object of the proposed invention is to provide a convenient and technological method of preparing an additive for lubricating materials based on chemically modified nanosized particles of molybdenum trisulfide and derivatives thereof.

#### Summary of the Invention

In order to realize the stated object, the instant method of preparing additives for lubricating materials is provided, with two embodiments realizing said method being proposed.

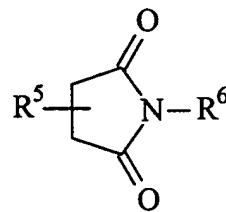
25 In accordance with the first embodiment, a method of preparing additives for lubricating materials based on chemically modified nanosized particles of molybdenum trisulfide and derivatives thereof comprises preparing the nanosized particles of molybdenum trisulfide and derivatives thereof from salts of thiomolybdic acid of the general formula  $\text{M}_2\text{MoS}_{4-x}\text{O}_x$ , where M is  $\text{NH}_4$ , Na, x is 0 – 3, in the presence of two modifiers, where tetraalkylammonium salts of 30 the general formula  $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{NX}$ , wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are identical or different and are independently selected from the group consisting of  $\text{C}_1\text{-C}_{16}$  alkyl, X is Cl or Br, or mixtures thereof are used as the first modifier, while derivatives of succinimide of the general formula



where  $R^5$  is normal or branched alkyl or oligoalkylene with a molecular weight of from 140 to about 1000,  $R^6$  is selected from the group consisting of H,  $-C(=O)NH_2$ ,  $-(CH_2CN_2NH)_nCH_3$ , n is 1 to 4, are used as the second modifier,

5 wherein said process is carried out by thermally processing a homogenized in a polar solvent mixture of said salt of thiomolybdic acid and said first or second modifier, cooling the obtained mixture and subsequently adding said second or first modifier, respectively.

The second embodiment of realizing the method according to the present invention consists in that the nanosized particles of molybdenum trisulfide and derivatives thereof are 10 prepared from salts of molybdic acid of the general formula  $M_2MoO_4$  where M is  $NH_4$ , Na, and a sulfur donor which is an inorganic sulfide or polysulfide of the general formula  $M'_2S_n$ , wherein M' is  $NH_4$ , Na, n is 1 to 4, or thiourea, in the presence of two modifiers, modifiers, where tetraalkylammonium salts of the general formula  $R^1R^2R^3R^4NX$ , wherein  $R^1$ ,  $R^2$ ,  $R^3$  and 15  $R^4$  are identical or different and are independently selected from the group consisting of  $C_1-C_{16}$  alkyl, X is Cl or Br, or mixtures thereof are used as the first modifier, while derivatives of succinimide of the general formula



where  $R^5$  is normal or branched alkyl or oligoalkylene with a molecular weight of from 140 to about 1000,  $R^6$  is selected from the group consisting of H,  $-C(=O)NH_2$ ,  $-(CH_2CN_2NH)_nCH_3$ , n 20 is 1 to 4, are used as the second modifier,

wherein the process is carried out by thermally processing a homogenized in a polar solvent mixture of said salt of molybdic acid, and said first or second modifier, cooling the obtained mixture and subsequently adding said second or first modifier, respectively.

In the proposed method, in accordance with any of the above embodiments, the thermal 25 processing is carried out at a temperature of 150 to 220°C for 1 to 2 hours, while methanol,

ethanol, propanol, isopropanol, n-butanol, isobutanol, 2-butanol, acetone or benzene is used as the solvent.

Tetraalkylammonium salt is selected from the group consisting of tricaprylmethylammonium chloride (Alikvat® 336), methyl-trialkyl(C<sub>8</sub>-C<sub>10</sub>)ammonium chloride (Adogen® 464), cetyl-trimethylammonium bromide (CTAB).

The product prepared by any variant of carrying out the method is filtered in order to isolate the solid admixtures and to remove the residues of volatile organic solvents under vacuum. The whole process of preparation may be carried out in one pot, without intermediate steps of isolating and/or purifying, without involving large amounts of organic solvents.

The prepared product is a viscous liquid of dark brown color, easily miscible with hydrocarbons and petroleum oils to form transparent solutions or compositions, which have a color from reddish-brown to brown. The content of molybdenum in the product is usually from 0.5 to 2.0 % by weight. Solutions of the obtained product are stable dispersions of surface-modified nanosized particles of molybdenum trisulfide, which is confirmed by data of electronic spectroscopy in the UV and visual region (Fig. 1) and a small-angle X-ray spread (SAXS) (Fig. 2). The SAXS method makes it possible to determine the dimensions of the inorganic core of the nanosized particles, which are within the range of from 1 to 6 nm and, as different from the surface-modified nanosized particles described in [7], are characterized by monodisperse size distribution. The latter circumstance makes it possible to presume a higher degree of reproducibility of the synthesis.

The examples below illustrate the instant invention, but do not in any manner limit the scope thereof in any way.

Example 1.

A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of methyltrialkyl(C<sub>8</sub>-C<sub>10</sub>)ammonium chloride (Adogen® 464) and 5 ml of methanol is subjected to thermal processing at 200°C for 2 hours, the product residue is 30% of the total starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered through a "blue belt" filter, the solvent is removed under vacuum. The content of molybdenum in the product is 1.22%. There are no absorption bands corresponding to ammonium tetrathiomolybdate in the UV spectrum of the prepared product.

Example 2.

A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of tricaprylmethylammonium chloride (Alikvat® 336) and 5 ml of

methanol is subjected to thermal processing at 200°C for 2 hours, the product residue is 29% of the total starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered as in Example 1, the solvent is removed under vacuum. The content of molybdenum in 5 the product is 1.25%.

Example 3.

A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of cetyltrimethylammonium bromide (CTAB) and 10 ml of a methanol-chloroform 1:1 mixture is subjected to thermal processing at 200°C for 2 hours, the 10 residue of the product is 55% of the total original weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 1.36%.

Example 4.

15 A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 1.5 g of CTAB and 1.5 g of Adogen® and 10 ml of a methanol-chloroform 1:1 mixture is subjected to thermal processing at 200°C for 2 hours, the product residue is 42% of the total starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, 20 filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 1.38%.

Example 5.

A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of Adogen® and 5 ml of methanol is subjected to thermal processing 25 at 180°C for 2 hours, the product residue is 29% of the starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 1.19%.

Example 6.

30 A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of Adogen® and 5 ml of methanol is subjected to thermal processing at 210°C for 2 hours, the product residue is 27.5% of the starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is

stirred with a magnetic stirrer, filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 1.25%.

Example 7.

5 A homogeneous mixture prepared by mixing at 60°C 0.24 g of ammonium tetrathiomolybdate, 3.0 g of Adogen® and 5 ml of acetone is subjected to thermal processing at 200°C for 2 hours, the product residue is 26.2% of the starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 2.92%.

10 Example 8.

A homogeneous mixture prepared by mixing at 60°C 0.12 g of ammonium tetrathiomolybdate, 3.0 g of Adogen® and 5 ml of methanol is subjected to thermal processing at 200°C for 2 hours, the product residue is 28.2% of the starting weight of the components. 4.2 g of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is 15 stirred with a magnetic stirrer, filtered, the solvent is removed under vacuum. The content of molybdenum in the product is 1.22%.

Example 9.

20 A homogeneous mixture prepared by mixing at 60°C 0.24 g of ammonium tetrathiomolybdate, 3.0 g of Adogen® and 5 ml of methanol is subjected to thermal processing at 200°C for 2 hours, the product residue is 30.1% of the original total weight of the components. 4.2 g of an N-alkylenamino derivative of alkenylsuccinimide and 5 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, the solvent is removed under. The content of molybdenum in the product is 1.19%.

Example 10.

25 The method of preparing according to Example 1, except for that ethanol is used instead of methanol.

Example 11.

The method of preparing according to Example 1, except for that propanol is used instead of methanol.

30 Example 12.

The method of preparing according to Example 1, except for that isopropanol is used instead of propanol.

Example 13.

The method of preparing according to Example 1, except for that n-butanol is used instead of methanol.

Example 14.

The method of preparing according to Example 1, except for that iso-butanol is used  
5 instead of methanol.

Example 15.

The method of preparing according to Example 1, except for that 2-butanol is used instead of methanol.

Example 16.

10 The method of preparing according to Example 9, except for that ammonium trithiomolybdate is used instead of ammonium tetrathiomolybdate.

Example 17.

The method of preparing according to Example 9, except for that ammonium dithiomolybdate is used instead of ammonium tetrathiomolybdate.

15 Example 18.

The method of preparing according to Example 9, except for that ammonium monothiomolybdate is used instead of ammonium tetrathiomolybdate.

Example 19.

20 A homogeneous mixture prepared by mixing at 60°C 0.0095 g of ammonium molybdate, 0.0113 g of Na<sub>2</sub>S·9H<sub>2</sub>O and 0.0360 g of Adogen® in 1 ml of benzene is subjected to thermal processing at 200°C for 30 minutes. The product residue after thermal processing is 48% of the total weight of the starting components. 0.0420 g of alkenylsuccinimide and 1 ml of chloroform are added to the product residue, the mixture is stirred with a magnetic stirrer, filtered through a "blue belt" filter, then the solvent is removed under vacuum. The content of  
25 molybdenum in the product is 1.35%.

Example 20.

30 The method of preparing according to Example 1, wherein at first 0.12 g of ammonium tetrathiomolybdate and 4.2 g of alkenylsuccinimide are homogenized, the mixture is subjected to thermal processing at 180-200°C for 1 hour, then 3.0 g of Adogen® are added to the residue, homogenized and subjected to thermal processing at 180 – 200°C during 1 hour. The residue is dissolved in chloroform, filtered, the solvent is removed under vacuum. As a result, a product is obtained with a molybdenum content of 0.66%.

Example 21.

A homogeneous mixture prepared by mixing at 60°C 0.0102 g of ammonium molybdate, 0.0320 g of Adogen®, 0.0101 g of thiourea and 5 ml of benzene is subjected to thermal processing at 200°C for 2 hours. The product residue after thermal processing is 43.0% of the total weight of the starting components. 5 ml of chloroform is added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, then the solvent is evaporated under vacuum. The content of molybdenum in the product is 2.35%.

Example 22.

A homogeneous mixture prepared by mixing at 60°C 0.0101 g of ammonium molybdate, 0.0315 g of Adogen®, 0.0145 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and 5 ml of benzene is subjected to thermal processing at 200°C for 2 hours. The product residue after thermal processing is 39.0% of the total weight of the starting components. 5 ml of chloroform is added to the product residue, the mixture is stirred with a magnetic stirrer, filtered, and then the solvent is evaporated under vacuum. The content of molybdenum in the product is 1.31%.

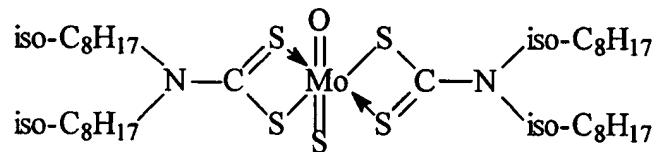
All the results are presented in Table 1.

The characteristics of samples of antifriction additives based on surface-modified nanosized particles of molybdenum trisulfide as prepared in Examples 1–22 are presented below.

Sample No.	Yield, wt. %	Concentration of molybdenum, wt. %	Ratio Mo:S, mole/mole	Average size of particles, angstrom
O-1	26.1	1.34	1:2.5	27.3
O-2	31.3	1.25	1:2.7	32.4
O-3	20.3	1.36	1:3.1	28.1
O-4	22.0	1.38	1:2.8	28.4
O-5	22.4	1.19	1:2.9	26.7
O-6	27.5	1.25	1:2.7	33.3
O-7	33.8	2.92	1:2.9	30.5
O-8	31.2	1.22	1:2.6	29.0
O-9	35.9	1.19	1:2.5	29.6
O-10	37.4	1.08	1:3.2	28.9
O-11	27.6	1.32	1:2.7	29.4
O-12	21.1	1.40	1:2.7	27.9
O-13	25.8	1.11	1:2.5	26.9
O-14	19.7	2.03	1:2.8	26.8
O-15	26.1	1.56	1:2.1	24.7
O-16	22.6	1.34	1:1.8	31.4
O-17	35.2	0.98	1:1.1	34.3
O-18	20.3	2.56	1:2.3	28.1
O-19	15.9	1.35	1:2.6	28.2
O-20	30.5	0.66	1:2.7	27.2
O-21	27.0	2.35	1:3.0	26.7
O-22	20.6	2.31	1:3.1	29.6

## TRIBOLOGICAL PROPERTIES OF PREPARED NANOSIZED PARTICLES

The tribological properties of the prepared antifriction additives based on surface-modified nanosized particles of molybdenum trisulfide were studied with respect to their composition in turbine oil T46 with the use of a vibrating tribometer SRV (Optimol firm, Germany). Test conditions: friction pair – ball-plane; amplitude of oscillations – 1 mm, frequency 50 Hz; axial load changes from 20 to 600 N step-by-step, 1 min at each step, the step being 50 N. The value of the coefficient of friction is measured, the test is considered to be finished in the case where the value of the coefficient of friction exceeds 0.22, or if there is a scratch (automatic stop). The oil compositions were prepared by mixing T46 with a 5 wt.% of samples O-1 to O-22. Surface-modified nanosized particles of molybdenum trisulfide, prepared in accordance with [7] (sample  $[\text{MoS}_x]$ ) and also molybdenum dithiocarbamate of formula III are used as a sample for comparison.



III

15

Data on tribologic tests conducted in respect to some samples are shown below.

Sample No.	Amount of Mo in oil, parts per million	Minimum coefficient of friction	Critical load, N
O-1	670	0.065	No
O-2	625	0.065	No
O-4	690	0.065	No
O-19	675	0.066	600
O-21	1175	0.060	No
sample $[\text{MoS}_x]$	650	0.065	600
Mo(III) dithiocarbamate	1000	0.067	550

Thus, the proposed method makes it possible to prepare an antifriction additive on the basis of surface-modified nanosized particles of molybdenum trisulfide, this additive forming transparent, stable dispersions in hydrocarbons and petroleum oils, and also effectively reducing the coefficient of friction between the metal surfaces and increasing the critical load of the solvents in vacuum. The whole process may be carried out in one pot without intermediate steps of isolating and/or purifying, without involving large amounts of organic solvents.

25 Sources of information, taken into account:

1. US Patent No. 4,400,282 (23 August 1983)
2. US Patent No. 4,474,673 (2 October 1984)
3. US Patent No. 4,765,918 (23 August 1988)
4. US Patent No. 6,117,826 (12 September 2000)
5. US Patent No. 6,245,725 (12 June 2001)
6. Great Britain Patent No. 2 359 092 (15 August 2001)
7. US Patent application WO 01/94504 A2 (13 December 2001)

Table 1

Example No.	Salt of thiomolybdc acid (amount, g)/solvent	Salt of quaternary ammonium base (amount, g)	Inorganic sulfide (amount, g)	Derivative of succinimide (amount, g)	Temperature of synthesis	
					Step 1, °C	Step 2, °C
1	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/no	Adogen® 464 (3.0)	No	II.1 (4.2)	60	200
2	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Alirkvat® 336 (3.0)	No	II.1 (4.2)	60	200
3	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	CTAB (3.0)	No	II.1 (4.2)	60	200
4	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	CTAB:Adogen 1:1 (3.0)	No	II.1 (4.2)	60	200
5	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	180
6	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	210
7	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.24)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	200
8	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Adogen (3.0)	No	II.2 (4.2)	60	200
9	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Adogen (3.0)	No	II.3 (4.2)	60	200
10	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/ethanol	Adogen (3.0)	No	II.1 (4.2)	60	200
11	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/propanol	Adogen (3.0)	No	II.1 (4.2)	60	200
12	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/isopropanol	Adogen (3.0)	No	II.1 (4.2)	60	200
13	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/n-butanol	Adogen (3.0)	No	II.1 (4.2)	60	200
14	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/isobutanol	Adogen (3.0)	No	II.1 (4.2)	60	200
15	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/2-butanol	Adogen (3.0)	No	II.1 (4.2)	60	200
16	(NH <sub>4</sub> ) <sub>2</sub> MoOS <sub>3</sub> (0.12)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	200
17	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>2</sub> S <sub>2</sub> (0.15)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	200
18	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>3</sub> S(0.21)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	200
19	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> S <sub>24</sub> (0.0095)/benzene	Adogen (0.03)	Na <sub>2</sub> S (0.0119)	II.1 (0.04)	60	200
20	(NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> (0.12)/methanol	Adogen (3.0)	No	II.1 (4.2)	60	200
21	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> (0.0095)/benzene	Adogen (0.03)	Thiourea (0.01)	II.1 (0.04)	60	200
22	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> (0.0095)/benzene	Adogen (0.03)	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 5H <sub>2</sub> O (0.01)	II.1 (0.04)	60	200